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#### (57) Abstract

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The present invention relates to a water-soluble transferable colorant composition which comprises a water soluble transfer material and a colorant wherein the transferable colorant is capable of transferring from a substrate and adhering to a receptor element upon the application of heat energy to the rear surface of the substrate, the transferable colorant strips from the front surface of the substrate when heated, the transferable colorant providing adherence to said receptor element by flowing onto said receptor element and solidifying thereon. The present invention further relates to a method of transferring the water-soluble transferable colorant composition to a receptor element.

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# TRANSFERABLE COLORANTS AND METHOD OF APPLYING AN IMAGE TO A RECEPTOR ELEMENT

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

The present invention relates to a transferable colorant composition per se, and to a method of 5 applying an imaqe to a receptor element. More specifically, the present invention relates transferable colorant composition that can be applied to various substrates, then optionally transferred to a receptor element using heat and pressure. The 10 transferable colorant compositions of the invention are of being directly transferred painting) to, for instance, a textile such as a shirt or the like without requiring the use of commercial equipment, such as video cameras, computers, color 15 copiers, home and/or lithographic printers.

## 2. Description of the Prior Art

Textiles such as shirts (e.g., tee shirts) having a variety of designs thereon have become very popular in recent years. Many shirts are sold with pre-printed designs to suit the tastes of consumers. In addition, many customized tee shirt stores are now in business which permit customers to select designs or decals of

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their choice. Processes have also been proposed which permit customers to create their own designs on transfer sheets for application to tee shirts by use of a conventional iron, such as described in U.S. Patent No. 4,244,358 issued September 23, 1980. Furthermore, U.S. Patent No. 4,773,953 issued September 27, 1988, is directed to a method for utilizing a personal computer, a video camera or the like to create graphics, images, or creative designs on a fabric.

U.S. Patent 5,620,548 is directed to a silver halide photographic transfer element and to a method for transferring an image from the transfer element to a receptor surface.

Provisional application 60/029,917 filed November 15 4, 1996 requires that silver halide light sensitive grains are dispersed within a carrier which functions as a transfer layer, and does not have a separate transfer layer.

Provisional Application Serial Number 60/030,933
20 filed November 15, 1996 is directed to a transfer element using CYCOLOR technology and to a method of transferring a developed image to a receptor surface, wherein the imaging system comprises a support, microcapsules, developer, and transfer material.

25 Provisional Application Serial Number 60/065,806 filed November 14, 1997 requires that the microcapsules and transfer material are in separate layers.

US Patents 4,185,957 and 4,139,343 disclose sublimation dyes in an ink base with ethyl cellulose.

30 In these patents, textiles are colored with waterinsoluble dyestuffs that undergo sublimation. The dye on the substrate is caused to sublime or be vaporized onto the surface of the textile to penetrate the fibers and to be entrained therein.

35 US Patent 5,269,865 discloses a transfer material and colorant for use in a thermal transfer recording

method capable of providing a recorded image, which is removable by lift-off correction, on a recording medium (i.e. paper).

U.S. Patent 5,487,614 discloses a transferable material containing heat activated, sublimation ink solids. The ink solids are transferred by means of a printer from a ribbon to a medium. The heat activated ink solids used do not have an affinity for highly absorbent fibers such as cotton. Thus, a printer ribbon panel having a polymeric coating thereon acts as a surface coating for the cotton component of the substrate. The heat sublimates the ink solids during the transfer from the medium to the substrate.

U.S. Patent 5,575,877 discloses a computer driven

means to print an image by means of selective transfer
of inks or dyes. An ink or dye is printed from a
ribbon to a medium. A 'polymeric surface preparation
material' is then printed over the design formed by
the ink or dye. Optionally, the surface preparation
material may be mixed with the ink formulation when,
for example, one or more of the panels of the ribbon
of the multiple pass thermal printer incorporates a
polymeric surface preparation material which is
printed onto the medium with the ink and binder.

U.S. Patents 5,268,052 and 4,870,427 disclose a thermal transfer of a thermoplastic ink formulation from a transfer sheet (ink ribbon) onto a receiver sheet. The ink ribbon contains thereon a heat-fusible binder such as wax and heat fusible resin.

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## SUMMARY OF THE INVENTION

The present invention relates to a water-soluble or dispersible transferable colorant composition, which comprises a water-soluble transfer material having a melting point of at least 65°C and comprising at least one of:

- (i) particles of a thermoplastic polymer having dimensions of about 1 to about 50 micrometers, from about 10 to about 50 weight percent of a film forming binder, based upon the weight of the thermoplastic 5 polymer, and optionally from about 0.2 to about 10 weight percent of a fluid viscosity modifier, based on the weight of the thermoplastic polymer;
- (ii) about 15 to about 80 percent by weight of a film-forming binder selected from the group consisting 10 of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 85 to about 20 percent by weight of a powdered thermoplastic polymer selected from the group consisting of polyolefins, polyesters, polyethylene, polyamides, waxes, ероху polymers, 15 ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the range of from about 65°C to about 180°C and the powdered thermoplastic polymer comprising particles of 20 about 1 to about 50 micrometers;
- (iii) a film forming binder selected from the group consisting of ethylene-acrylic acid copolymers having particles of about 1 to about 50 micrometers, polyolefins, and waxes and which melts in the range of from about 65°C to about 180°C;
- (iv) a thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers and which melts in 30 the range of from about 65°C to about 180°C;
- (v) a thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers, ethylene-35 methacrylic acid copolymers, and ethylene-acrylic acid

copolymers and which melts in the range of from about  $65^{\circ}$ C to about  $180^{\circ}$ C; or

(vi) a natural wax.

The water-soluble or dispersible transferable colorant composition further comprises a water soluble or dispersible colorant.

The present invention further relates to a method of applying an image to a receptor element which comprises the steps of:

- 10 (A) applying the water-soluble or dispersible transferable colorant composition of the present invention to a substrate;
- (B) positioning a surface of said substrate having the transferable colorant composition thereonagainst said receptor element; and
  - (C) applying heat to the rear surface of said substrate to transfer said transferable colorant composition to said receptor element.

The present invention further comprises a kit 20 comprising:

- (A) at least one container having a watersoluble or dispersible transferable colorant composition;
- (B) at least one application means for applying25 said transferable colorant composition to a substrate;and
  - (C) optionally at least one substrate and/or at least one receptor element.

The present invention further relates to a method 30 of applying an image to a receptor element that comprises the steps of:

- (A) applying a water-soluble or dispersible colorant composition to a receptor element;
- (B) positioning a surface of a non-stick sheet 35 against said receptor element over the area on which

said water-soluble colorant composition was applied, and;

- applying heat to the rear surface of said (C) non-stick sheet; and
- removing said non-stick sheet from said 5 receptor element.

## BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully detailed description 10 understood from the given hereinbelow, and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, and wherein:

FIGURE 1 illustrates the ink transfer procedure 15 wherein the transferable colorant composition releases from the substrate upon the application of heat and pressure, and is transferred onto the receptor element; and

FIGURE 2 illustrates the step of ironing the 20 substrate which is positioned onto a tee shirt or the like.

### DETAILED DESCRIPTION OF THE INVENTION

In order to attract the interest of consumer 25 groups that are already captivated by the tee shirt rage described above, the present inventors provide the capability of transferring images created by the directly to a receiver element using owner transferable colorant. A unique advantage of 30 invention is to enable all consumers to wear and display on apparel designs created themselves and to do so in the single most cost and time efficient means.

This invention entails the creation of a colorant 35 (e.g. ink) that can be applied to various substrates and then transferred to a receptor element using heat

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(e.g. from a household hand-held iron) and pressure (e.g. typical pressure used when ironing in, instance, a circular motion). In one embodiment, the transferable colorant composition comprises a 5 dispersion with a thermoplastic polymer/colorant complex. In this embodiment, the wax dispersion and thermoplastic polymer/colorant components combine to form a liquid, aqueous phase. The liquid, phase is applied to a substrate using any type of 10 application device (e.g. an ink jet printer, paintbrush, Magic Marker, pen, etc.). The applied liquid is preferably allowed to dry completely prior to subsequent processing in order to avoid smudging of the image. The dry image is placed image side down on 15 a receptor. Heat and pressure are applied to the nonimage side of the substrate until transfer complete. Transfer under the conditions described herein usually occurs after heat and pressure are applied (i.e. approximately 30 seconds). The substrate 20 is then removed from the receptor.

In another embodiment of the present invention, a transferable colorant composition comprises a transfer material that has a melting point of at least 65°C, preferably at least 100°C, and a colorant. Said transfer material is capable of transferring and adhering the transferable colorant composition of the invention from a front surface of a substrate support upon the application of heat energy to the rear surface of the substrate, said transfer composition 30 strips from said front surface of the substrate by liquefying and releasing from said substrate when heated. said liquefied transferable colorant composition providing adherence to a receptor element by flowing onto said receptor element and solidifying 35 thereon. The particle size of the transfer material is

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from 1 to 50 micrometers, preferably 2 to 50 micrometers, and more preferably 1 to 20 micrometers.

The receptor surface or element for the image may be a textile such as a shirt (e.g. tee shirt) or the like. Other suitable receptor surfaces include but are not limited to metals, leather, canvas, paper, glass, ceramic, wool, cotton fabric, cotton blend fabric, plastic or receptor supports used by the museum or conservatory industry. Energy applied to the rear surface of the substrate is heat and/or pressure (e.g. via ironing such as by a household iron or commercial heat press).

The present invention also relates to a method of applying a transferable colorant composition to a receptor element, which comprises the steps of:

- (a) applying a transferable colorant composition comprising the transfer material and colorant of the invention to a substrate, said transfer material being capable of transferring and adhering applied areas from 20 said front surface of said substrate upon the application of heat energy to the rear surface of the substrate, said transfer composition and colorant strips from said front surface of the substrate by liquefying and releasing from said substrate when 25 heated, the liquefied transferable colorant composition providing adherence to a receptor element by flowing onto said receptor element and solidifying thereon, said adherence does not require an external adhesive layer;
  - (b) positioning the front surface of said substrate against said receptor element; and
  - (c) applying energy (e.g. heat) to the rear surface of the substrate to transfer said transferable colorant composition to said receptor element.
- Accordingly, the transferable colorant composition of the invention is capable of transferring and

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adhering from the front surface of the substrate upon the application of heat energy to the rear surface of the substrate. The transferable colorant composition strips from said front surface of the substrate by liquefying and releasing from the substrate when heated. The liquefied transfer material provides adherence to a receptor element by flowing onto the receptor element and solidifying thereon. The adherence does not require an external adhesive layer.

10 In description, the term transferable colorant composition refers to (i) a wax dispersion and/or a thermoplastic polymer, and (ii) colorant mixture. Substrate refers to any substance onto which the transferable colorant composition is applied, such 15 as paper. The receptor refers to any object onto which the dried transferable colorant composition (on the substrate) is transferred. "TPP" is used to refer to a thermoplastic polymer of the invention. Colorant is used to describe any pigment or dye used to color a 20 substance. The colorant is preferably not a sublimation dye. The term "release" indicates a 50-100% transfer of the colorant composition from the substrate to the receptor element. Preferably "release" is 65-100% transfer, more preferably 70-100%.

The transferable colorant composition preferably 25 adheres to fibrous supports, polymer films (e.g. polyethylene), and optionally to glassy metal supports. Additionally, there should be color saturation (significant color gain relative to the 30 original image), good resolution and edge definition with little or no degradation as a result of the transfer. That is, color saturation, in the transfer, should be equal to or greater than the color saturation found in the original image. The transferable colorant 35 composition should have good transferability, soft hand, and washability (e.g., preferably 3,

preferably 5+ washes). Hand is defined as the texture of a fabric as perceived by touch or manual manipulation. Soft hand is a texture, or perceived feel by hand, which is similar to, or identical to the original substrate or material.

The transferable colorant composition of the invention should also be capable of transfer from the substrate and adhere to a receptor element without the requirement of a separate surface adhesive layer.

10 Without being bound by any theory, upon back surface heating of the substrate, the transferable colorant composition undergoes a solid to solution phase transition resulting in a transfer to the receptor element. Adhesion to the receptor element would occur upon cooling of the transferable colorant composition onto the receptor element. Upon cooling, an image would be transferred onto the receptor element.

Suitable transfer materials include wax dispersions derived from but not limited to natural 20 waxes such as carnauba wax, mineral waxes, montan wax, derivatives of montan wax, petroleum waxes, synthetic waxes such as polyethylene and oxidized polyethylene waxes. Suitable transfer materials further include compositions comprising materials from U.S. 25 Patent Nos. 5,501,902, 5,271,990 and 5,242,739. The contents of U.S. Patent Nos. 5,501,902, 5,271,990 and 5,242,739 are herein incorporated by reference. These patents are discussed in turn hereinbelow.

The transfer material of the present invention may 30 utilize the materials of the second layer of U.S. Patent No. 5,501,902.

Thus, the transfer material of the present invention preferably includes particles of a thermoplastic polymer having largest dimensions of less than about 50 micrometers, and preferably from about 1 to about 20 micrometers. The particles will more

preferably have dimensions of from about 2 to about 10 micrometers. In general, the thermoplastic polymer can be any thermoplastic polymer which meets the criteria set forth herein. Desirably, the powdered thermoplastic 5 polymer will be selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl copolymers. However, the thermoplastic preferably excludes tackifiers such as alicyclic hydrocarbons, terpene, or rosin. Tackifiers are heat 10 activated resins used to solidify an image on printed Tackifiers generally refer to convertible polymer systems upon the application of energy, such as heat. Resins and rosins tend to irreversibly harden upon the application of heat energy. Therefore, 15 tackifiers tend to be more like thermosetting materials rather than thermoplastic materials. Therefore, most preferably, the transfer material of the invention includes polymers that are thermoplastic in nature rather thermosetting-type than materials (e.g. thermosetting tackifiers).

The transfer material also includes from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer. Desirably, the amount of binder will be from about 10 to about 30 weight percent. In general, any binder may be employed which meets the criteria set forth herein. When the transfer material of the invention includes a cationic polymer, a nonionic or cationic dispersion or solution may be employed as the binder. The binder desirably will be heat softenable at temperatures of about 120° Celsius or lower.

When the transferable colorant composition is intended to be used as a heat-transfer material, the transfer material will have a melting point of from about 65 to about 180 degrees Celsius. The term "melts" and variations thereof are used herein only in a

qualitative sense and are not meant to refer to any particular test procedure. Reference herein to a melting temperature or range is meant only to indicate an approximate temperature or range at which a polymer or binder melts and flows under the conditions of a melt-transfer process to result in a substantially smooth film.

Manufacturers' published data regarding the melt behavior of polymers or binders correlate with the 10 melting requirements described herein. It should be noted, however, that either a true melting point or a softening point may be given, depending on the nature of the material. For example, materials such as polyolefins and waxes, being composed mainly of linear polymeric molecules, generally melt over a relatively narrow temperature range since they are somewhat crystalline below the melting point.

points, if not provided Melting by the manufacturer, are readily determined by known methods 20 such as differential scanning calorimetry. and especially copolymers, are amorphous polymers, because of branching in the polymer chains or the sidechain constituents. These materials begin to soften and flow more gradually as the temperature is increased. It 25 is believed that the ring and ball softening point of such materials, as determined by ASTM E-28, is useful in predicting their behavior. Moreover, the melting points or softening points described are better indicators of performance than the chemical nature of 30 the polymer or binder.

The transfer material desirably also will contain from about 2 to about 20 weight percent of a cationic polymer, based on the weight of the thermoplastic polymer. The cationic polymer may be, for example, an amide-epichlorohydrin polymer, polyacrylamides with cationic functional groups, polyethyleneimines,

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polydiallylamines, and the like. When a cationic polymer is present, a compatible binder should be selected. The binder desirably will be a nonionic binder, either in the form of a solution or a nonionic or cationic dispersion or emulsion. As is well known in the paper coating art, many commercially available binders have anionically charged particles or polymer molecules. These materials are generally not compatible with the cationic polymer which may be used in the present invention.

One or more other components may be used in the transfer material. For example, the transfer material may contain from about 1 to about 20 weight percent of a humectant, based on the weight of the thermoplastic 15 polymer. Desirably, the humectant will be selected from the group consisting of ethylene glycol and poly(ethylene glycol). The poly(ethylene glycol) typically will have a weight average molecular weight of from about 100 to about 40,000. A poly(ethylene 20 glycol) having a weight-average molecular weight of from about 200 to about 800 is particularly useful.

The transfer material also may contain from about 0.2 to about 10 weight percent of a fluid (e.g. ink) viscosity modifier, based on the weight of the thermoplastic polymer. The viscosity modifier desirably will be a poly(ethylene glycol) having a weight-average molecular weight of from about 100,000 to about 2,000,000. The poly(ethylene glycol) desirably will have a weight-average molecular weight of from about 100,000 to about 100,000 to about 600,000.

Other components which may be present in the transfer material include from about 0.1 to about 5 weight percent of a weak acid and from about 0.5 to about 5 weight percent of a surfactant, both based on the weight of the thermoplastic polymer. A particularly useful weak acid is citric acid. The term "weak acid"

is used herein to mean an acid having a dissociation constant less than one (or a negative log of the dissociation constant greater than 1).

The surfactant may be an anionic, a nonionic, or a cationic surfactant. When a cationic polymer is present in the transfer layer, the surfactant should not be an anionic surfactant.

Desirably, the surfactant will be a nonionic or cationic surfactant. However, in the absence of the 10 cationic polymer, an anionic surfactant may be used, if desired. Examples of anionic surfactants include, among linear and branched-chain others. alkylbenzenesulfonates, linear and branched-chain alkyl sulfates, and linear and branched-chain alkyl ethoxy 15 sulfates. Cationic surfactants include, by way of trimethylammonium tallow chloride. illustration, Examples of nonionic surfactants, include, again by way alkyl polyethoxylates, illustration only, polyethoxylated alkylphenols, fatty acid ethanol 20 amides, complex polymers of ethylene oxide, propylene oxide, and alcohols, and polysiloxane polyethers. More surfactant will be desirably, the surfactant.

Heat transfer of the transferable colorant composition of the present invention may be by any known means, such as by lasers, other infrared emitting devices, a hand-held iron or a heat transfer press. The transfer temperature typically will be from about 80° to about 120° Celsius, preferably from 100° to about 120° Celsius, for from about 5 seconds to about 2 minutes.

Accordingly, the transfer material of the invention may comprise particles of a thermoplastic polymer preferably having largest dimensions of less than about 50 micrometers, preferably from about 1 to

about 20 micrometers, and more preferably from about 2 to about 10 micrometers, from about 10 to about 50 weight percent of a film-forming binder, based on the weight of the thermoplastic polymer, and from about 0.2 to about 10 weight percent of a viscosity modifier, based on the weight of the thermoplastic polymer.

The transfer material has a melting point of more than 65°C, preferably more than 100°C and preferably from about 100 to about 180 degrees Celsius. 10 The transfer material may also contain from about 2 to about 20 weight percent of a cationic polymer, based on the weight of the thermoplastic polymer. The transfer material may also contain from about 1 to about 20 weight percent of a humectant, based on the weight of 15 the thermoplastic polymer. The humectant may be (1) ethylene glycol or (2) polyethylene glycol (e.g. having a weight-average molecular weight of from about 100 to about 40,000, preferably about 200 to about 800).

The viscosity modifier may be a polyethylene glycol having a weight average molecular weight of from 100,000 to about 2,000,000, preferably from about 100,000 to about 600,000. The viscosity modifier may be low or high viscosity methyl cellulose or polyvinyl alcohol.

The transfer material may also include about 0.1 to about 5 weight percent of a weak acid, based on the weight of the thermoplastic polymer. The transfer layer may also include about 0.5 to about 5 weight percent of a surfactant (e.g. nonionic or cationic), based on the weight of the thermoplastic polymer.

The transfer material may further comprise from about 1 to about 20 weight percent of a humectant, based on the weight of the thermoplastic polymer (and optionally from about 0.2 to about 10 weight percent of a fluid (e.g. ink) viscosity modifier, based on the weight of the thermoplastic polymer), and from 0.5 to

about 5 weight percent of a surfactant, based on the weight of the thermoplastic polymer.

The transfer material of the present invention may also utilize the materials of the image receptive melttransfer film layer of U.S. Patent 5,271,990.

Thus, the transfer material of the present invention may be comprised of a thermoplastic polymer which melts at above 65°C, preferably above 100°C, and more preferably in the range of from about 100 to about 100 degrees Celsius(°C). In another embodiment, the thermoplastic polymer melts in the range of from about 80°C to 120°C, preferably from 100°C to about 120°C.

In general, any known thermoplastic polymer can be employed so long as it meets the criteria specified 15 herein. Preferably, the thermoplastic polymer is selected from the group consisting of polyolefins, polyesters, and ethylene-vinyl acetate copolymers, having a particle size of less than 50 micrometers, preferably having a particle size of less than 20, and 20 more preferably less than 10 micrometers.

The transfer material of the present invention may also utilize the materials of the image-receptive melt-transfer film layer of U.S. Patent 5,242,739.

Thus, the transfer material may comprise from 25 about 15 to about 80 percent by weight of a filmforming binder selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, waxes and from about 85 to about 20 percent by weight of a powdered thermoplastic polymer selected from the 30 group consisting of polyolefins, polyesters, polyamides, waxes, epoxy polymers, ethylene-acrylic acid copolymers, and ethylene-vinyl acetate copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts above about 65°C, 35 preferably above about 100, and more preferably in the

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range of from about 100 to about 180 degrees Celsius and said powdered thermoplastic is preferably of particles which are from about 1 to about 50 micrometers in diameter, preferably about 2 to 50, and 5 more preferably 1 to about 20 micrometers in diameter.

Accordingly, the transfer material comprises from about 15 to about 80 percent by weight of a filmforming binder and from about 85 to about 20 percent by weight of a powdered thermoplastic polymer. Each of the 10 film-forming binders and powdered thermoplastic polymers melt above 65°C, preferably above 100°C, and more preferably in the range of from about 100 to about 180 degrees Celsius (°C). In addition, the powdered thermoplastic polymer is preferably composed 15 particles having diameters of about 50 micrometers, more preferably from about 2 to 50 micrometers, and most preferably from about 1 to about 20 micrometers.

In other embodiments, each of the film-forming binders and powdered thermoplastic polymers melt in the range from 80°C to above 120°C, preferably in the range of from about 100°C to about 120°C.

A function of the powdered thermoplastic polymer is to assist in the transferring of the colorant composition to a fabric, both in terms of ease of transfer and the permanence of the transferred image. Additionally, the thermoplastic polymer, when combined with the colorant, provides a more homogenous ink.

The nature of the film-forming binder is not known to be critical. That is, any film-forming binder can be employed so long as it meets the criteria specified herein. In preferred embodiments, the film-forming binder has, at the transfer temperature, a lower melt viscosity than the powdered thermoplastic polymer. As a practical matter, water-dispersible ethylene-acrylic

acid copolymers have been found to be especially effective film forming binders.

Accordingly, the transfer material may comprise a polymer selected from the thermoplastic group 5 consisting of polyolefins, polyesters, and ethylenevinyl acetate copolymers and which melts above 65°C, and preferably above 100°C, and more preferably in the range of from about 100 to about 180 degrees Celsius, and most preferably in the range of about 100 to about 10 120 degrees Celsius. The thermoplastic polymers used in invention can formulations of the thermoplastic polymer derived from a group including but not limited to polyolefins, polyesters, oxidized polyethylene, polyacrylates, polyethylene, ethylene-vinyl 15 ethylene-acrylate and copolymers. The thermoplastic polymer should have a softening point ranging from 70° to 150°C, preferably 108°C. Additionally, chemically modified thermoplastic polymers may be added to bind polar dyes 20 for the same application.

The powdered thermoplastic polymers, upon melting, flow partially into the fiber matrix of the fabric to which an image is being transferred. The result is a fabric having an image which does not render the fabric stiff. Moreover, the image itself is neither rubbery nor rough to the feel and is stable to repeated washings.

As a general rule, the amount of powdered thermoplastic polymer employed can be reduced if larger 30 particle sizes are employed.

If desired, the transfer material can contain other materials, such as processing aids, release agents, pigments, deglossing agents, antifoam agents, and the like. The use of these and other like materials is well known to those having ordinary skill in the art. However, organic solvents such as toluene and

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methyl isobutyl ketone should be excluded transferable colorant compositions of the present invention. Toluene, for example, is a known vehicle for ink. However, toluene should be specifically excluded 5 from the present invention because (1) it is a known carcinogen and toxic substance, and (2) incompatible with water-dissolved polymers and colorants used in the present invention.

Representative binders and powdered thermoplastic 10 polymers are as follows:

#### Binder A

Binder A is Michem® 58035, supplied by Michelman, Inc., Cincinnati, Ohio. This is a 35 percent solids dispersion of Allied Chemical's AC 580, which is approximately 10 percent acrylic acid and 90 percent ethylene. The polymer reportedly has a softening point of 102°C and a Brookfield viscosity of 0.65 pas (650 centipoise) at 140°C.

20 Binder B

This binder is Michem® Prime 4983R (Michelman, Inc., Cincinnati, Ohio). The binder is a 25 percent solids dispersion of Primacor® 5983 made by Dow Chemical Company. The polymer contains 20 percent acrylic acid and 80 percent ethylene. The copolymer has a Vicat softening point of 43°C and a ring and ball softening point of 100°C. The melt index of the copolymer is 500 g/10 minutes (determined in accordance with ASTM D-1238).

30 Binder C

Binder C is Michem® 4990 (Michelman, Inc., Cincinnati, Ohio). The material is 35 percent solids dispersion of Primacor® 5990 made by Dow Chemical Company. Primacor® 5990 is a copolymer of 20 percent acrylic acid and 80 percent ethylene. It is similar to

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Primacor® 5983 (see Binder B), except that the ring and ball softening point is 93°C. The copolymer has a melt index of 1,300 g/10 minutes and Vicat softening point of 39°C.

5 Binder D

This binder is Michem® 37140, a 40 percent solids dispersion of a Hoechst-Celanese high density polyethylene. The polymer is reported to have a melting point of 100°C.

10 Binder E

This binder is Michem® 32535 which is an emulsion of Allied Chemical Company's AC-325, a high density polyethylene. The melting point of the polymer is about 138°C. Michem® 32535 is supplied by Michelman, Inc., Cincinnati, Ohio.

#### Binder F

Binder F is Michem® 48040, an emulsion of an Eastman Chemical Company microcrystalline wax having a melting point of 88°C. The supplier is Michelman, Inc., 20 Cincinnati, Ohio.

#### Binder G

Binder G is Michem® 73635M, an emulsion of an oxidized ethylene-based polymer. The melting point of the polymer is about 96°C. The hardness is about 4-6 Shore-D. The material is supplied by Michelman Inc., Cincinnati, Ohio.

## Powdered Thermoplastic Polymer A

This powdered polymer is Microthene® FE 532, an ethylene-vinyl acetate copolymer supplied by Quantum Industries, Cincinnati, Ohio. The particle size is reported to be 20 micrometers. The Vicat softening point is 75°C and the melt index is 9 g/10 minutes.

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## Powdered Thermoplastic Polymer B

Powdered Thermoplastic Polymer B is Aqua Polysilk 19. It is a micronized polyethylene wax containing some 5 polytetrafluoroethylene. The average particle size is 18 micrometers and the melting point of the polymer is 102°-118°C. The material is supplied by Micro Powders, Inc., Scarsdale, N.Y.

Powdered Thermoplastic Polymer C

This material is Microthene® FN-500, a low density polyethylene powder supplied by USI Chemicals Co., Cincinnati, Ohio. The material has a particle size of 20 micrometers, a Vicat softening point of 83°C, and a melt index of 22 g/10 minutes.

## Powdered Thermoplastic Polymer D

This polymer is Aquawax 114, supplied by Micro Powders, Inc., Scarsdale, N.Y. The polymer has a 20 reported melting point of 91°-93°C and an average particle size of 3.5 micrometers; the maximum particle size is stated to be 13 micrometers.

## Powdered Thermoplastic Polymer E

- Powdered Thermoplastic Polymer E is Corvel<sup>®</sup> 23-9030, a clear polyester from the Powder Coatings Group of the Morton Chemical Division, Morton Thiokol, Inc., Reading, Pa.
- Powdered Thermoplastic Polymer F

  This material is Corvel® natural nylon 20-9001, also supplied by Morton Thiokol, Inc.

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Powdered Thermoplastic Polymer G

This polymer powder is Corvel® clear epoxy 139020, supplied by Morton Thiokol, Inc.

Powdered Thermoplastic Polymer H

Powdered Thermoplastic Polymer H is AClyn® 246A,

which has a melting temperature of about 95°C as

determined by differential scanning calorimetry. The

polymer is an ethylene-acrylic acid magnesium ionomer.

The material is supplied by Allied-Signal, Inc.,

Morristown, N.J.

Powdered Thermoplastic Polymer I

This polymer is AC-316A, an oxidized high density
15 polyethylene. The material is supplied by Allied
Chemical Company, Morristown, N.J.

Powdered Thermoplastic Polymer J

This polymer is Texture 5380, supplied by Shamrock

Technologies, Inc., Newark, N.J. It is powdered polypropylene having a melting point of 165°C and an average particle size of 40 micrometers.

The binders and thermoplastic polymers may be 25 combined and blended as desired. For example, Binder A 80 parts) may be blended with powdered thermoplastic polymer A (e.g. 80 parts) and optionally with a fluorocarbon dispersion such as Zonyl 7040 (e.g. 0.20 parts) obtained from duPont. Another example 30 includes combining Binder B (e.g. 400 parts) Polymer B (e.g. 70 parts) and blending in a standard laboratory colloid mill. Also, Binder A (e.g. parts) may be combined with Polymer C (e.g. 65 parts). Binder B (e.g. 400 parts) may be combined with Polymer 35 D (e.g. 70 parts). Binder C (e.g. 200 parts) may be combined with Polymer E (e.g. 35 parts) and optionally

with propylene glycol (e.g. 20 parts) and water (e.g. 20 parts). Similarly, Binder C (e.g. 200 parts) may be combined with Polymer F (e.g. 54 parts) and optionally with propylene glycol (e.g. 20 parts) and water (e.g. 5 20 parts). Also, Binder A (e.g. 200 parts) may be combined with Polymer G (e.g. 30 parts) and optionally with propylene glycol (e.g. 20 parts) and water (e.g. 20 parts). Binder D (e.g. 200 parts) may be combined with Polymer H (e.g. 30 parts) and optionally water 10 (e.g. 40 parts) and blended. Binder A (e.g. 286 parts) may be combined with Polymer J (e.g. 40 parts) and optionally with propylene glycol (e.g. 50 parts).

In the transferable colorant composition of the present invention, various dyes or pigments generally 15 used in the field of printing and recording may be used as the colorant. Colorants, for the purposes of this invention, include all inks, dyes, and pigments used in printing, imaging, and/or craft applications. Thus, colorants include, but are not limited to azo dyes, 20 anthraquinone, food coloring dyes, cyclic or polycyclic aromatic compounds, organic and inorganic colorants, and metallic compounds. Examples of colorants include ink jet inks, finger paints, and watercolors. However, the colorants of the present invention are not heat-25 activated or sublimated during the transfer process. Accordingly, the transferable colorant composition preferably does not contain heat-activated or sublimation dyes.

Specific examples of the colorant may be one or more of known dyes or pigments such as Carbon black, Pearl All-Surface paint, LUMA water colors, LeFranc & Bourbeois Flashe vinyl colors paint, Winsor & Newton Designers Gouache. The colorants used in the present invention may include dyes and pigments that can be water dissolved or dispersed with or without a polymer additive. Companies that manufacture these colorants

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include BASF, Sun Chemical, Flint Ink, Aldrich, DuPont, Eastman Kodak, Hewlett Packard, Canon (and Ilford, manufacturers), other ink printer jet Pearl, ArtistColor, Koh-I-Noor, Higgins, Rotring, 5 Yarka, Hansa, Luma, Lefranc & Bourgeois, Crayola, and Windsor & Newton.

The wax dispersion provides the colorant with its ability to flow from the substrate to the receptor. Ultimately the wax dispersion provides the adhesion of 10 the colorant to the receptor. In another embodiment of the invention, in addition to helping provide a more homogeneous ink, a thermoplastic polymer is added along the wax to provide water resistance, enhances the washability of the colorant on 15 receptor.

The transferable colorant composition application method requires an application device and a substrate that will accept the colorant composition. Application devices include but are not limited to paintbrushes, 20 rubberstamps, ink dispensing writing tools, ink-jet printers, and bubble-jet printers. Substrates include but are not limited to laser copier acetate, write-on acetate, ink-jet acetate, plain copier paper, and card stock paper.

The function of the substrate is to provide a surface that will provide ink adhesion as well as 50-100% release, preferably 70-100% release, and most preferably 90-100% release. Fibrous substrates tend to absorb large amounts of the transferable colorant providing adequate 30 composition without Plastic-like substrates provide adequate characteristics, but do not always provide adequate ink Acetate (Apollo Apollo Laser Copier adhesion. Presentation Products, Ronkonkoma, N.Y.) and Apollo 35 Write-On Acetate display the best characteristics, providing even transfer and soft hand.

The only noticeable drawback to the Apollo Write-On Acetate is the low melting point. The acetate melted at the same temperature as the colorant composition. This problem is resolved by placing an intermediate sheet (e.g. plain paper) between the acetate and a transfer device such as a handheld iron or a heat press.

Another suitable substrate includes a support coated with the second layer disclosed in U.S. Patent 5,798,179, but without the third and fourth layers 10 disclosed therein. Similarly, another suitable substrate is а material comprising support ("substrate") and barrier layer disclosed in copending provisional application 60/127,625 to Williams et al. filed on April 1, 1999, but without the release layer 15 and image receiving layer disclosed therein. Still another suitable substrate is disclosed in copending provisional application no. 60/130,500 to Williams filed on April 23, 1999, and in copending provisional application no. 60/133,861 to Williams filed on May 12, 20 1999. Specifically, suitable substrates include the ("substrate") and barrier layer of these support provisional applications, but without the layer, optional image receiving layers, and/or optional antistatic layers. All of these sheets have the 25 advantage that the transferable colorant composition of the invention should not penetrate into the paper stock due to the presence of the barrier layer. These sheets should allow virtually all of the transferable colorant composition to transfer to the receptor element.

30 Representative acetates are as follows:

## Substrate A

3M Write-On Transparency Film is a clear film manufactured by 3M that is used with transparency marking pens.

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## Substrate B

Apollo Write-On Transparency Film is a clear film manufactured by Apollo that is used with transparency marking pens.

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#### Substrate C

Apollo Laser Copier Transparency Film is a clear film manufactured by Apollo that is used with most laser printers.

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#### Substrate D

Apollo Ink Jet Transparency Film is a clear film manufactured by Apollo that is used with most Hewlett Packard ink jet printers.

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#### Substrate E

Hewlett Packard Glossy Photo Paper is a gloss coated fibrous paper manufactured by Hewlett Packard that is used with most Hewlett Packard ink jet printers.

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#### Substrate F

Union Camp Frankote 12pt Coated Cover is a gloss coated fibrous paper manufactured by Union Camp that I used in offset lithography applications.

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### Substrate G

Wausau 60lb Card Stock is a heavy fibrous paper manufactured by Wausau that is used in a variety of applications.

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### Substrate H

Plain Copy Paper is a fibrous paper used in a variety of applications.

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One preferred application of this invention is for the transferable colorant composition to be applied with a brush using methods such as freehand painting, a stencil, and painting-by-numbers. tracing, 5 embodiment, the transferable colorant composition could be packaged in a crayon-type set (e.g. a kit), or as a mixture where colorant and/or water is added upon use. Optionally, the mixture may be packaged concentrated form. The concentrated form may be a paste 10 or gel. An example of a concentrate (paste or gel) can be made by the following formulation: 1 part Michem Emulsion 73635, and 1 to 3 parts thermoplastic polymer/colorant mixture. This formulation range may be modified as necessary to form a concentrate of the 15 consistency of "toothpaste."

The kit may comprise the transferable colorant composition of the invention, an application means for applying the colorants to a substrate (e.g. paintbrush, pen), and optionally substrate sheets and/or receiving elements.

Another embodiment of this invention is for the transferable colorant composition to be applied with an ink-jet printer. In this application, the transferable colorant composition is applied to the substrate by the printer and printing the image onto the substrate.

Another embodiment of this invention is for the transferable ink to be applied with a pen (e.g. a "paint pen") or rubberstamp.

In another embodiment of the invention, the transferable composition is directly applied onto the receptor element. Then, the composition is driven into the receptor element with an iron, wherein a non-stick sheet (i.e. silicon sheet) is inserted between the iron and the face of the receptor element containing the composition prior to ironing. Since the transferable

composition is capable of surviving washing, the composition may be used directly as a paint.

transferable colorant composition invention may be prepared as follows: a thermoplastic 5 polymer that meets the criteria set forth herein is combined with a colorant to provide a homogenous composition. Water is measured into a beaker. colorant is suspended in the water by stirring until colorant is dispersed in the water. 10 thermoplastic polymer is added to the water. thermoplastic polymer repels the water while attracting the colorant particles. Once the thermoplastic polymer and colorant particles are completely combined, the mixture is filtered (i.e. poured through a Whatman #1 15 filter or a comparable paper filter). The supernatant is then collected and the thermoplastic polymer and colorant are allowed to thoroughly dry to form a homogenous mixture. One (1) to three (3) parts (by volume) Michem® 73653M wax dispersion, which meets the 20 criteria set forth herein, is mixed with one (1) part colorant/ thermoplastic polymer, as described, instance, in Formulation 2, until a homogenous mixture The emulsion is obtained. wax and colorant/thermoplastic polymer are stirred (i.e. with a 25 spatula for approximately one minute to break down any large particles, then placed in a beaker with a stirring flea on a stirring plate) until a homogenous mixture is obtained.

The following examples are provided for a further 30 understanding of the invention, however, the invention is not to be construed as being limited thereto.

#### Example 1

A transferable ink of the invention is prepared as 35 follows: one part (weight) Microthene FE 532-00 (a

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thermoplastic polymer) is combined with 0.25 to 1.5 parts (weight) Sunfast Blue 249-2083 (a colorant) to provide a homogenous composition. Water is measured into a beaker. The Sunfast Blue 249-2083 colorant is suspended in the water by rapid stirring until the colorant is dispersed in the water.

#### Formulation 1

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## Colorant/TPP Compound

		<del>504.14</del>		
	Components	<u>Parts</u>		
15	Colorant (Sunfast Blue 249-2083, Sun Chemical)	0.25 to 1.5 parts (weight)		
	TPP (Microthene FE 532-00, Quantum)	1 part (weight)		
20	Water	4 parts (volume)		

Microthene FE 532-00 is slowly added to the water. The thermoplastic polymer repels the water while attracting the colorant particles. Once the Microthene 25 FE 532-00 and Sunfast Blue 249-2083 are completely combined, the mixture is poured through a Whatman #1 filter or a comparable paper filter. The supernatant is then collected and the Microthene FE 532-00 and Sunfast Blue 249-2083 are allowed to thoroughly dry to form a 30 homogenous mixture. One (1) to three parts (3) volume) Michem® 73635M wax dispersion, which meets the criteria set forth herein, is mixed with one (1) part colorant/thermoplastic polymer, described as Formulation 2, until a homogenous mixture is obtained.

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#### Formulation 2

## Transferable Ink Mixture

5	Components	Parts			
	Colorant/TPP Mixture	1 to 3 parts (weight)			
10	Wax Dispersion (Michem 73635M, Michelman)	1 part (volume)			

The emulsion wax and colorant/thermoplastic polymer are stirred (i.e. with a spatula for approximately one minute to break down any large particles, then placed in a beaker with a stirring flea on a stirring plate) until they form a homogenous solution.

The prepared transferable colorant composition is more viscous than water and has less surface tension than water.

## EXAMPLE 2

To apply the transferable colorant composition to the substrate, paint brush is coated with а 25 transferable colorant composition. The transferable colorant composition is then applied to the substrate. The composition is then allowed to dry completely. Referring to Figure 1, there is generally illustrated the ink transfer procedure. In step 1, the substrate 20 30 is placed colorant composition 10 side against a receptor element 30. Acetate is used as the substrate 20. Optionally, a plain sheet of paper is placed over the acetate substrate to prevent the substrate from melting. A transfer device (e.g. hand iron or a heat 35 press) is used to apply heat to the substrate (step 2) which in turn releases the colorant composition 10. The temperature transfer range of the hand iron is 100° to 200°C with 110°C being the preferred temperature. The heat press operates at a temperature transfer range of

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100°C to 220°C with 190°C being the preferred temperature. The hand iron, when used as the transfer device, is placed over the non-colorant composition side (i.e. the back side) of the substrate and moved in a circular motion. Slight pressure is applied as the heating device is moved over the substrate 20. After 30 seconds of heat and pressure, the transfer device is removed from the substrate. The substrate 20 is then peeled away from the receptor 30 (step 3). The image is allowed to cool, which provides for proper image setting.

#### EXAMPLE 3

This Example evaluates various ratios of wax to colorant/TPP. Although different ratios of wax to colorant/TPP were able to transfer, 1.25 to 1.5 parts wax to 1 part colorant/TPP provides the best transfer results.

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# Evaluation of Transferability between Various Mixture Ratios

## (3M Write-on Acetate, 1.5 mil coat)

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Mixture Ratio	Transfer		
Wax:Colorant/TPP	Device	Transferability	Hand
1:1	Hand Iron (110°C)	Slightly uneven transfer, ≈50% release	Rough, plastic feel
1:1	Heat Press (190°C)	Slightly uneven transfer, ≈50% release	Rough, plastic feel
1.25 : 1	Hand Iron (110°C)	Good, even transfer, ≈85% release	Soft, plastic feel
1.25 : 1	Heat Press (190°C)	Slightly uneven transfer, ≈80% release	Soft, plastic feel
1.5 :1	Hand Iron (110°C)	Slightly uneven transfer, ≈75% release	Slightly Rough
1.5 :1	Heat Press (190°C)	Good, even transfer, ≈80% release	Slightly Rough
2:1	Hand Iron (110°C)	Uneven transfer, ≈60% release	Rough, plastic feel
2:1	Heat Press (190°C)	Even transfer, ≈75% release	Slightly Rough
3:1	Hand Iron (110°C)	Uneven transfer, ≈40% release	Rough
3:1	Heat Press (190°C)	Good, even transfer, ≈70% release	Soft

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The 1:1 ratio has the relatively least desirable results due to poorer ink release from the substrate as well as poorer adhesion to the receptor. The higher concentrated wax mixtures are unable to transfer as evenly due to poorer release characteristics. The 1.25 and 1.5 mixtures allow up to 85% of the ink mixture to release from the substrate, which is distributed evenly across the receptor. The even distribution of ink provides a uniform surface on the receptor which gives the ink a softer hand.

#### EXAMPLE 4

This Example evaluates various substrates. The function of the substrate is to provide a surface that will provide ink adhesion as well as, for instance, 65-100% release. Plastic-like substrates provide adequate release characteristics, but do not always provide adequate ink adhesion.

Although the Apollo laser copier acetate and write-on acetate displayed the best transfer characteristics, providing even transfer and soft hand, the acetate melted at the same temperature as the ink. To remedy this problem, an intermediate sheet of plain paper is placed between the acetate and the transfer device. A plain sheet of paper is thus optionally used with all other acetates as a precautionary measure.

-34Evaluation of Transferability

Between Various Substrates

	Transfer		
Substrate	Device	Transferability	Hand
3M Write-On	Hand Iron	Good, even	Soft, fair
Acetate	(110°C)	· · · · · •	fabric
Acetate	(110 C)	transfer, ≈80%	penetration
		release	
3M Write-On	Heat	Good, even	Soft, fair
Acetate	Press	transfer, ≈85%	fabric
	(190°C)	release	penetration
Apollo	Hand Iron	Very good, even	Soft, good
Write-On	(110°C)	transfer, ≈85%	fabric
Acetate		release	penetration
Apollo	Heat	Excellent, even	Soft,
Write-On	Press	transfer, ≈90%	excellent
Acetate	(190°C)	release	fabric
	\	lerease	penetration
Apollo	Hand Iron	Very good, even	Soft, good
Laser	(110°C)	transfer, ≈80%	fabric
Copier	'	release	penetration
Acetate		Terease	*
Apollo	Heat	Very good, even	Soft, very
Laser	Press	transfer, ≈85%	good fabric
Copier	(190°C)	release	penetration
Acetate	1		
Apollo Ink	Hand Iron	Uneven transfer,	Rough, less
Jet Acetate	(110°C)	≈60% release	fabric
			penetration
Apollo Ink	Heat	Good, even	Soft, fair
Jet Acetate	Press	transfer, ≈75%	fabric
	(190°C)	release	penetration
HP Glossy	Hand Iron	Uneven transfer,	Soft, less
photo paper	(110°C)	≈30% release	fabric
-			penetration
HP Glossy	Heat	Good, even	Soft, less
photo paper	Press	transfer, ≈65%	fabric
	(190°C)	release	penetration
Union Camp	Hand Iron	Slightly uneven	Soft, good
Frankote	(110°C)	transfer, ≈70%	fabric
		release	penetration
Wausau Card	Hand Iron	Slightly uneven	Slightly
Stock	(110°C)	transfer, ≈65%	rough, fair
,		release	fabric
			penetration
<u> </u>	<del></del>		

Substrate	Transfer Device	Transferability	Hand
Wausau Card Stock	Heat Press (190°C)	Very good, even transfer, ≈70% release	Soft, very good fabric penetration
Plain Copier Paper	Hand Iron (110°C)	Good, even transfer, ≈75% release	Soft, good fabric penetration
Plain Copier Paper	Heat Press (190°C)	Very good, even transfer, ≈75% release	Soft, excellent fabric penetration

#### EXAMPLE 5

Referring to Figure 2, a method of transferring the colorant composition to a receptor element will be described. More specifically, Figure 2 illustrates how the step of heat transfer of the colorant composition from the substrate (50) to a tee shirt or fabric (62) is performed.

The transferable colorant composition is prepared, and is applied to the substrate as in Examples 1-3. A tee shirt (62) is laid flat, as illustrated, on an appropriate support surface, and the front surface of the substrate (50) is positioned onto the tee shirt. A sheet of plain copy paper is optionally placed over the substrate for precautionary measures. A household iron (64) set at its highest heat setting is run and pressed across the back (52A) of the substrate. The colorant composition is transferred to the tee shirt and the support is removed and discarded.

#### EXAMPLE 6

This example evaluates various combinations of wax binders. Michem® wax Emulsion 58035 and Michem® Prime 4983R are used as the transfer materials. The following colorants are tested:

Paint A. Pearl All-Surface Paint is a permanent water based fabric paint manufactured by Pearl that can used on a wide variety of substrates.

Paint B. Luma Brilliant Concentrated Water Color is a concentrated ink manufactured by Luma that can be diluted in water and used on a wide variety of substrates.

Paint C. Lefranc & Bourgeous Vinyl Colors is a vinyl based paint manufactured by Lefranc & Bourgeous 10 that can be thinned in water and used on a variety of substrates.

Paint D. Windsor & Newton Designers Gouache is a gum arabic and pigment based paint manufactured by Windsor & Newton that can be used on a wide variety of substrates.

The mixtures appearing in the Table below are applied to transparent acetate substrates, unsized copy paper, and sized paper by dipping a natural bristle paintbrush into the paint mixture. A Meyer rod was used to apply thinner coatings (0.4-1.5 mils) onto the substrates. All coatings were allowed to air dry for 10 minutes prior to transfer.

Transfer is successful upon application of heat and pressure. Both a heat press and a hand iron (individually) are used and obtained similar results. 80-100% of coatings transfers from acetate substrate to T-shirt receptor element (50/50 blend) upon applying 180°C for 20 seconds with high, constant pressure from the back surface of the substrate. Sized paper releases approximately 50% of its coating upon transfer. Although the transfer is less than 100%, the color and texture remained satisfactory. Unsized copy paper transfers approximately 60%-75% of the coating, which is adequate.

Coating color intensity remains unchanged during the transfer process. When higher transfer temperatures

are used, a color shift occurs in paints due to instability in the pigments.

A standard machine wash using a normal cycle is followed using TIDE® detergent to determine washability. About 10% color loss occurs during washing. All transferred samples retain edges during wash, felt soft to the touch, and return to their original position after being pulled.

All mixtures displayed ease of coating, acceptable color intensity, and excellent wash characteristics when 66% - 84% of Binder A is added to 8% - 17% paint, and 8%-17% Binder B.

<u> </u>	8 E003E	8 40025	9. Dedent	D1
Paint	<u>% 58035</u>	% 4983R	% Paint	Results and
				Observations
A	66.7	16.6	16.7	Shiny liquid. Opaque.
1				95% transfer, excellent
				wash.
A	83.3	8.3	8.4	Transparent hue.
]	ŀ			Bubbles upon coating.
				Solidifies. Less edge
				retention. 100%
Ì	[		ļ.	transfer, excellent
<u> </u>				wash.
A	83.3	0	16.7	Opaque. Lower
		İ	ł	viscosity. Does not
				solidify as thoroughly.
ļ				Less edge retention.
			1	100% transfer. Loses
			l	15-20% when washed.
A	0	16.6	83.4	Slight transparency.
		1	1	50% transfer. Loses 15%
L		]		in wash.
С	66.7	16.6	16.7	Similar viscosity to
1	]	1	1	unaltered paint.
	Ì	1		Excellent hue, chroma
	,			production. Opaque.
1				Solidifies after 2
	<u>L</u>			minutes. 100% transfer.
C	83.3	8.3	8.4	Bubbles form upon
1	1			application, less edge
ł		1		retention. 80%
				transfer.
В	83.3	8.3	8.4	Less color intensity.
				100% transfer.
D	83.3	8.3	8.4	Less color strength.
ł				90% transfer. Good
				hand. No cracking. No
L	<u> </u>		L	peeling.

### EXAMPLE 7

In this example, a transferable colorant mixture is made without Binder B as described in Example 6, above. A TPP which meets the criteria set forth in the specification is used to enhance water resistance upon transfer. 50% (w/w) of Microthene Powder FE 532 is added to 50% Michem wax Emulsion 58035 (40g total). 4ml of Paint B are added, and optionally allowed to mix in a stir plate, followed by 5 minutes mixing by a sonic

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dismembrating horn. Upon painting and drying, the paint is a powder texture on the top from the TPP. After the above-discussed transfer techniques are followed, 80% to 90% transfer results.

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## EXAMPLE 8

A transferable colorant composition is prepared in accordance with Example 1 using a mixture of Michem® 58035 and Michem® Prime 4983 as the wax dispersion 10 (binder). Both materials are available from Michelman, Inc., Cincinnati, Ohio. A ratio of four or five to one of 58035 to 4983 is used. The basis weight of the melttransfer layer is 8  $g/m^2$ . Michem® 58035 is a 35 percent solids dispersion of Allied Chemical's AC 580, which is 15 approximately 10 percent acrylic acid and 90 percent ethylene. The polymer reportedly has a softening point of 102°C. and a Brookfield viscosity of 0.65 Pas (650 centipoise) at 140°C. Michem® Prime 4983 is a 25 percent solids dispersion of Primacor®5983 made by Dow 20 Chemical Company. The polymer contains 20 percent acrylic acid and 80 percent ethylene. The copolymer has a Vicat softening point of 43°C. and a ring and ball softening point of 100°C. The melt flow rate of the copolymer is 500 g/10 minutes.

When the thermoplastic binder and/or the binder are the variables, the cationic polymer in every case is an amide-epichlorohydrin copolymer, namely, either Kymene® 557 or Reten® 204LS, both being supplied by Hercules Inc., Wilmington, Del. The cationic polymer is included at a level of 5 weight percent, based on the weight of the thermoplastic polymer.

In general, a minimum amount of binder is used. For example, 10 weight percent of a polyacrylate, Rhoplex® B-15 (Rohm and Haas Company) may be used.

35 Another binder which may be used at the 10 weight

percent level is Michem® 58035, described above. The binder must be compatible with the cationic polymer. Two binders which are more compatible with the cationic polymer and which yellow less than the Michem® 58035 are Airflex® 124 and Airflex® 125, both poly(vinyl alcohol) stabilized ethylene-vinyl acetate copolymers. The materials are available from Air Products and Chemicals, Inc., Allentown, Pa.

Several thermoplastic polymers may be used including Microthene® FE 532, an ethylene-vinyl acetate copolymer supplied by USI Chemicals Co., Cincinnati, Ohio. The particle size is reported to average approximately 20 micrometers. The Vicat softening point is 75°C. The melt flow rate of the copolymer is 9 g/10 minutes and it is reported to have a density of 0.928 g/cm³. Another thermoplastic polymer is Microthene® FN 500, a low density polyethylene powder also supplied by USI Chemicals Co. The material has an average particle size of 20 micrometers, a Vicat softening point of 83°C., a melt flow rate of 22 g/10 minutes, and a density of 0.915 g/cm³.

The composition is applied to a substrate, allowed to dry, and transferred as in Example 3.

#### 25 EXAMPLE 9

Example 8 is repeated, but using the following thermoplastic polymers:

Thermoplastic Polymer A

This polymer is Microthene® FE 532.

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## Thermoplastic Polymer C

Thermoplastic Polymer C is Corvel® 2093. It is a polyester. The average particle size is 20 micrometers, the melting point of the polymer is approximately 80°C., and the melt flow rate is reported to be "high". The material is supplied by Powder Coatings Group of the Morton Chemical Division, Morton Thiokol, Inc., Reading, Pa.

10 Thermoplastic Polymer D

This polymer is MP 22, a micronized polyethylene wax from Micro Powders, Inc., Scarsdale, N.Y. It has a reported melting point of 104°C, an average particle size of 4 micrometers, and a "high" melt flow rate.

15

## Thermoplastic Polymer E

Thermoplastic Polymer E is MPP 611 is also from Micro Powders, Inc. It has a reported melting point of 110°C, an average particle size of 6 micrometers, and a 20 "high" melt flow rate.

## Thermoplastic Polymer F

This material is MPP 635, also a polyethylene supplied by Micro Powders, Inc. The average particle size of the polymer is 5 micrometers, the melting point is reported to be 124, and the melt flow rate is "high".

## Thermoplastic Polymer G

This polymer is Accumist® B6, supplied by Allied Chemical Company, Morristown, NJ. The polymer is a polyethylene having a melting point of 126°C. The average particle size of the polymer is 6 micrometers and the melt flow rate is "high."

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#### Thermoplastic Polymer H

Thermoplastic Polymer H is Accumist® B12, also supplied by Allied Chemical Company. The polymer is a high density polyethylene having a melting point of 126°C. The average particle size of the polymer is 12 micrometers.

#### Thermoplastic Polymer I

This polymer is DPP 714, a polystyrene dispersion 10 supplied by Dow Chemical Company, Midland, Mich.

#### Thermoplastic Polymer J

This material is Piccotex® LC55R, a styrene-methyl styrene copolymer dispersion supplied by Hercules, Inc.

15

#### Thermoplastic Polymer K

Thermoplastic Polymer K is DL 256, a polystyrene dispersion also supplied by Dow Chemical Company.

### 20 Thermoplastic Polymer L

This polymer is BN 4901X, a polystyrene dispersion available from BASF Corporation, Sarnia, Ontario, Canada.

#### 25 Thermoplastic Polymer M

This material is Ropaque®, a polystyrene dispersion supplied by Rohm and Haas Company, Philadelphia, Pa.

30 Four different binders are used:

### Binder A

Binder A is Carboset® 514H, a polyacrylate binder dispersed in water, supplied by B.F. Goodrich Company, 35 Cleveland, Ohio.

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Binder B

This binder is Rhoplex® B15, described in Example 8.

5 Binder C Binder C Binder C is Michem<sup>®</sup> 58035.

Binder D

This binder is Marklube® 542, a cationic low 10 density polyethylene emulsion from Ivax Industries, Inc., Rock Hill, S.C.

The composition of the transfer material is summarized in Table 1 below. In the Table, the "TPP" column identifies the thermoplastic polymer by letter. The letter corresponds to the TPPs listed in this Example, and does not correspond to the lettered TPPs as previously described. The "Type" column identifies the binder by letter, and basis weights are given in g/m². The letters correspond to the binders listed in this Example, not the binders listed in the Specification as previously described.

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TABLE 1
Summary of Transfer Material Composition with Various Thermoplastic Polymers

•	with \	Binder			
5	TPP	Type	Wt.8	Basis Weight	
	A	A	10	21	
	A	В	10	23	
	A	С	10	23	
	Α	С	20	. 23	
10	В	С	50	31	
	В	С	10	23.	
	C	С	10	32	
	D	C .	10	30	
	E	C ,	10	23	
15	E	С	12.5	28	
	E	С	12.5	8	
	E	С	12.5	13	
	F	, <b>C</b>	10	23	
	F	С	12.5	13	
20	F	С	18	11	
	F	С	20	13	
	F	D	25	13	
	G	С	18	13	
	Н	C -	18	13	
25	I	C	10	17	
	J	С	10	17	
	K	C	10	8	
	L	С	10	8	
	M	С	10	8	
30	M	С	30	8	
	M	С	40	8	

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#### EXAMPLE 10

This Example evaluates various cationic polymers. Two types of transfer materials are employed, in which the cationic polymer is included as a component. Type A 5 consists of Microthene® FE 532 (Thermoplastic Polymer A), 13 weight percent of Michem® 58035 binder (Binder C), based on the weight of the thermoplastic polymer, 1 weight percent Triton® X-100 surfactant, cationic polymer. The basis weight of the layer is 15 10  $q/m^2$ . The type B material consists of MPP (Thermoplastic Polymer F), 18 weight percent of Michem® 58035 binder (Binder C), based on the weight of the thermoplastic polymer, 1 weight percent Triton® X-100 surfactant, and the cationic polymer. The basis weight 15 of the layer is 13  $g/m^2$ . The various cationic polymers evaluated are as follows:

#### Cationic Polymer A

Cationic Polymer A is Kymene® 557, an amide-20 epichlorohydrin copolymer available from Hercules, Inc.

#### Cationic Polymer B

This polymer is Calgan® 261LV, a quaternary polymer. It is available from Calgon Corporation.

25

#### Cationic Polymer C

This material is Corcat<sup>®</sup> P145. It is a polyethyleneimine supplied by Cordova Chemical Company.

30 Cationic Polymer D

Cationic Polymer D is Parez® 631NC, a polyacrylamide available from American Cyanamide.

#### Cationic Polymer E

This material is Betz<sup>®</sup> 1260. It is obtained from Betz Paperchem, Trevose, Pa.

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## Cationic Polymer F

This polymer is Reten® 204LS, an amide-epichlorohydrin copolymer available from Hercules, Inc.

5

Cationic Polymer G

Verona ® C-300 from Miles Inc., Pittsburgh, Pa.

Cationic Polymer H

10 Aquaprox<sup>®</sup> UP103 from Synthron, Morgantown, N.C.

Cationic Polymer I

Tinofix® EW from Ciba-Geigy Corporation, Hawthorn, N.Y.

15

Cationic Polymer J

Reactofix® ES from Ivax Industries, Inc.

Cationic Polymer K

20 Protefix® TS, a cationic carbamide from Synthron.

In the table, the column "CP Type" identifies the cationic polymer, whereas the column "Type" identifies the type of transfer material employed, as described above.

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TABLE 4
Evaluation of Various Cationic Polymers

	Evaluation of	various	Cationic	Polymers
	CP Type	Amount	Туре	
5	A	2	A	
	A	4	A	
	A	6	A	
	В	2	A	
	В	4	. <b>A</b>	
10	С	2	A	
	С	4	A	
	, <b>D</b>	2	A	
	D	4	A	
	E	2	A	
15	F	- 5	A	
	F	4	A	
	F	8	A	
	G	8	В	
	Н	8	В	
20	I	8	В	
	J	8	В	
	K	8	В	

The transferable colorant composition is applied 25 to a substrate, allowed to dry, and transferred as in Example 3.

## EXAMPLE 11

The formulations involving Cationic Polymer F as

30 reported in Example 10 are modified further since yellowing may be encountered when images are heat transferred.

In the experiments, the binder employed in the transfer layer is either Airflex<sup>®</sup> 124 (Binder E) or 35 Airflex 125<sup>®</sup> (Binder F). The binder is present at a level of 26 weight percent, based on the weight of the

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thermoplastic polymer. The cationic polymer used is Reten® 204LS, the humectant is Polyglycol® E200, a poly(ethylene glycol) from Dow Chemical Company having a weight-average molecular weight of about 200; the 5 humectant level is 10 weight percent, based on the weight of the thermoplastic polymer. The surfactant is Triton® X-100 at a level of 3 weight percent, based on the weight of thermoplastic polymer employed. The fluid viscosity modifier is Polyox® N80 at a level of 3 10 weight percent, also based on the weight of the thermoplastic polymer. The thermoplastic polymers to be evaluated include micropowders MPP 635 and Accumist® A-12, from Micropowders and Allied Chemical Company, respectively. The transferable colorant composition 15 comprising the above transfer material is applied to a substrate, allowed to dry, and transferred as Example 3.

The experiments are summarized in Table 5. In the table, the "TPP" column identifies the thermoplastic 20 polymer by letter (see Example 9), the "WT.-% CP" column identifies the amount of Reten® 204LS employed in the second layer in weight percent, based on the weight of the thermoplastic polymer, and the "WT.-% Acid" column identifies the amount of citric acid included in the transfer layer, in weight-percent based on the weight of the thermoplastic polymer.

TABLE 5
Summary of Cationic Polymer F
Formulation Modifications

30					
	Sample	Binder	TPP	Parts CP	Wt% Acid
	1	. <b>F</b>	H	. 8	None
	2	F	Н	8	4
	3	E	H	. 8	None
35	4	F	F	8	None
	5	F	F	12	None
	6	F	F	16	None

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All cited patents, publications, copending applications, and provisional applications referred to in this application are herein incorporated by reference.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the present invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

#### WHAT IS CLAIMED IS:

1 1. A water-soluble or dispersible transferable 2 colorant composition, which comprises:

a water-soluble transfer material having a 3 melting point of at least 65°C and comprising at least one of (i) particles of a thermoplastic polymer having dimensions of about 1 to about 50 micrometers, from about 10 to about 50 weight percent of a film forming binder, based upon the weight of the thermoplastic polymer, and optionally from about 0.2 to about 10 9 weight percent of a fluid viscosity modifier, based on 10 the weight of the thermoplastic polymer, (ii) about 15 to about 80 percent by weight of a film-forming binder 13 selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 15 85 to about 20 percent by weight of a powdered 16 thermoplastic polymer selected from the consisting of polyolefins, polyesters, polyethylene, waxes, epoxy polymers, polyamides, 18 ethylene-acrylic 19 copolymers, and ethylene-vinyl 20 copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the range of from about 65°C to about 180°C and the 22 powdered thermoplastic polymer comprising particles of 23 about 1 to about 50 micrometers, (iii) a film forming 24 binder selected from the group consisting of ethyleneacrylic acid copolymers having particles of about 1 to 27 about 50 micrometers, polyolefins, and waxes and which 28 melts in the range of from about 65°C to about 180°C, 29 (iv) a thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group 30 consisting of polyolefins, polyesters, and ethylenevinyl acetate copolymers and which melts in the range of from about 65°C to about 180°C, (v) a thermoplastic polymer having particles of about 1 to about 50

- 35 micrometers selected from the group consisting of
- 36 polyolefins, polyesters, and ethylene-vinyl acetate
- 37 copolymers, ethylene-methacrylic acid copolymers, and
- 38 ethylene-acrylic acid copolymers and which melts in
- 39 the range of from about 65°C to about 180°C; or (vi) a
- 40 natural wax; and
- 41 b) a water soluble or dispersible colorant with
- 42 the proviso that said colorant is not a sublimation
- 43 dye or heat activation dye.
- 1 2. The transferable colorant composition of claim 1,
- 2 wherein the transfer material comprises particles of a
- 3 thermoplastic polymer having dimensions of about 1 to
- 4 about 50 micrometers, from about 10 to about 50 weight
- 5 percent of a film-forming binder, based on the weight
- 6 of the thermoplastic polymer, and optionally from about
- 7 0.2 to about 10 percent of a fluid viscosity modifier,
- 8 based on the weight of the thermoplastic polymer.
- 1 3. The transferable colorant composition of claim 1,
- 2 wherein the transfer material comprises particles of a
- 3 thermoplastic polymer having dimensions of about 1 to
- 4 50 micrometers, from about 10 to about 50 weight
- 5 percent of a film-forming binder, based on the weight
- 6 of the thermoplastic polymer, and from about 2 to about
- 7 20 weight percent of a cationic polymer, based on the
- 8 weight of the thermoplastic polymer.
- 1 4. The transferable colorant composition of claim 1,
- 2 wherein the transfer material comprises from about 15
- 3 to about 80 percent by weight of a film-forming binder
- 4 selected from the group consisting of ethylene-acrylic
- 5 acid copolymers, polyolefins, and waxes and from about
- 6 85 to about 20 percent by weight of a powdered
- 7 thermoplastic polymer selected from the group
- 8 consisting of polyolefins, polyesters, polyamides,

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- 9 waxes, epoxy polymers, ethylene-acrylic acid
- 10 copolymers, and ethylene-vinyl acetate copolymers,
- 11 wherein each of said film-forming binder and said
- 12 powdered thermoplastic polymer melts in the range of
- 13 from about 65 to about 180 degrees Celsius and said
- 14 powdered thermoplastic consists of particles which are
- 15 from about 1 to about 50 micrometers in diameter.
  - 1 5. The transferable colorant composition of claim 1,
- 2 wherein the transfer material comprises a film-forming
- 3 binder selected from the group consisting of ethylene-
- 4 acrylic acid copolymers of about 1 to 50 micrometers,
- 5 polyolefins, and waxes and which melts in the range of
- 6 from about 65 to about 80 degrees Celsius.
- 1 6. The transferable colorant composition of claim 1,
- wherein the transfer material comprises a
- 3 thermoplastic polymer having particles of about 1 to
- 4 50 micrometers selected from the group consisting of
- 5 polyloefins, polyesters, and ethylene-vinyl acetate
- 6 copolymers and which melts in the range of from about
- 7 65 to about 180 degrees Celsius.
- 1 7. The transferable colorant composition of claim 1,
- 2 wherein said colorant is present in an amount of 0.25
- B to 1.5 parts (weight) to about 1 part (weight)
- 4 thermoplastic polymer.
- 1 8. The transferable colorant composition of claim 1,
- 2 wherein said colorant and said thermoplastic polymer
- 3 taken together are present in an amount of one part
- 4 (weight) of colorant/ thermoplastic polymer to about
- 5 1-3 parts (volume) film-forming binder.
- The transferable colorant composition of claim 8,
- 2 wherein said colorant and said thermoplastic polymer

- 3 taken together are present in an amount of 1 part
- 4 (weight) of colorant/thermoplastic polymer to about 1
- 5 part (volume) film-forming binder.
- 1 10. The transferable colorant composition of claim 8,
- 2 wherein said colorant and said thermoplastic polymer
- 3 taken together are present in an amount of 1 part
- 4 (weight) of colorant/thermoplastic polymer to about
- 5 1.25 parts (volume) film-forming binder.
- 1 ll. The transferable colorant composition of claim 8,
- 2 wherein said colorant and said thermoplastic polymer
- 3 taken together are present in an amount of 1 part
- 4 (weight) of colorant/thermoplastic polymer to about
- 5 1.5 parts (volume) film-forming binder.
- 1 12. The transferable colorant composition of claim 8,
- 2 wherein said colorant and said thermoplastic polymer
- 3 taken together are present in an amount of 1 part
- 4 (weight) of colorant/thermoplastic polymer to about 2
- 5 parts (volume) film-forming binder.
- 1 13. The transferable colorant composition of claim 8,
- 2 wherein said colorant and said thermoplastic polymer
- 3 taken together are present in an amount of 1 part
- 4 (weight) of colorant/thermoplastic polymer to about 3
- 5 parts (volume) film-forming binder.
- 1 14. The transferable colorant composition of claim 1,
- 2 which comprises:
- 3 a) a water-soluble transfer material having a
- 4 melting point of at least 65°C and comprising particles
- 5 of a thermoplastic polymer having dimensions of about
- 6 1 to about 50 micrometers, from about 10 to about 50
- 7 weight percent of a film forming binder, based upon
- 8 the weight of the thermoplastic polymer, and

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- optionally from about 0.2 to about 10 weight percent
- of a fluid viscosity modifier, based on the weight of
- the thermoplastic polymer; and
- 12 b) a water soluble or dispersible colorant.
  - 15. The transferable colorant composition of claim 1,
  - which comprises:
  - a) a water-soluble transfer material having a 3
  - melting point of at least 65°C and comprising about 15
  - to about 80 percent by weight of a film-forming binder
  - selected from the group consisting of ethylene-acrylic
  - 7 acid copolymers, polyolefins, and waxes and from about
  - 8 85 to about 20 percent by weight of a powdered
  - thermoplastic polymer selected from the
- consisting of polyolefins, polyesters, polyethylene,
- polyamides, waxes, epoxy polymers, ethylene-acrylic
- ethylene-vinyl 12 acid copolymers, and
- 13 copolymers, wherein each of said film-forming binder
- 14 and said powdered thermoplastic polymer melts in the
- range of from about 65°C to about 180°C and the
- powdered thermoplastic polymer comprising particles of
- about 1 to about 50 micrometers; and 17
- 18 b) a water soluble or dispersible colorant.
  - The transferable colorant composition of claim 1,
- 2 which comprises:
- a) a water-soluble transfer material having a 3
- melting point of at least 65°C and comprising a film
- forming binder selected from the group consisting of
- ethylene-acrylic acid copolymers having particles of
- about 1 to about 50 micrometers, polyolefins, and 7
- waxes and which melts in the range of from about 65°C
- to about 180°C; and
- a water soluble or dispersible colorant. 10

- 1 17. The transferable colorant composition of claim 1,
- 2 which comprises:
- 3 a) a water-soluble transfer material having a
- 4 melting point of at least 65°C and comprising a
- 5 thermoplastic polymer having particles of about 1 to
- 6 about 50 micrometers selected from the group
- 7 consisting of polyolefins, polyesters, and ethylene-
- 8 vinyl acetate copolymers and which melts in the range
- 9 of from about 65°C to about 180°C; and
- b) a water soluble or dispersible colorant.
- 1 18. The transferable colorant composition of claim 1,
  2 which comprises:
- 3 a) a water-soluble transfer material having a
- 4 melting point of at least 65°C and comprising a
- 5 thermoplastic polymer having particles of about 1 to
- 6 about 50 micrometers selected from the group
- 7 consisting of polyolefins, polyesters, and ethylene-
- 8 vinyl acetate copolymers, ethylene-methacrylic acid
- 9 copolymers, and ethylene-acrylic acid copolymers and
- 10 which melts in the range of from about 65°C to about
- 11 180°C; and
- b) a water soluble or dispersible colorant.
- 1 19. The transferable colorant composition of claim 1,
- 2 which comprises:
- 3 a) a water-soluble transfer material having a
- 4 melting point of at least 65°C and a natural wax; and
- 5 b) a water soluble or dispersible colorant.
- 1 20. The transferable colorant composition of claim 1,
- 2 which comprises said transferable colorant composition
- 3 in a dry or concentrated form.
- 1 21. The transferable colorant composition of claim
- 2 20, wherein said dry or concentrated form is a gel or

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- 3 paste comprising 1 part wax dispersion and 1 to 3
- parts thermoplastic polymer/colorant mixture.
- The transferable colorant composition of claim 1, 22.
- with the proviso that said water-soluble transferable
- colorant composition does not contain an organic
- solvent.
- dispersible transferable Α water-soluble or
- colorant composition, which comprises:
- a water-soluble transfer material having a 3
- melting point of at least 65°C and comprising at least
- one of (i) particles of a thermoplastic polymer having 5
- dimensions of about 1 to about 50 micrometers, from
- about 10 to about 50 weight percent of a film forming
- binder, based upon the weight of the thermoplastic
- polymer, and optionally from about 0.2 to about 10
- weight percent of a fluid viscosity modifier, based on
- the weight of the thermoplastic polymer, (ii) about 15
- to about 80 percent by weight of a film-forming binder
- selected from the group consisting of ethylene-acrylic
- acid copolymers, polyolefins, and waxes and from about
- 85 to about 20 percent by weight of a powdered 15
- thermoplastic polymer selected from
- consisting of polyolefins, polyesters, polyethylene, 17
- polyamides, waxes, epoxy polymers, ethylene-acrylic
- ethylene-vinyl and acid copolymers, 19
- copolymers, wherein each of said film-forming binder
- and said powdered thermoplastic polymer melts in the
- range of from about 65°C to about 180°C and the 22
- powdered thermoplastic polymer comprising particles of 23
- about 1 to about 50 micrometers, (iii) a film forming 24
- 25 binder selected from the group consisting of ethylene-
- acrylic acid copolymers having particles of about 1 to
- about 50 micrometers, polyolefins, and waxes and which 27
- melts in the range of from about 65°C to about 180°C,

- 29 (iv) a thermoplastic polymer having particles of about
- 30 1 to about 50 micrometers selected from the group
- 31 consisting of polyolefins, polyesters, and ethylene-
- 32 vinyl acetate copolymers and which melts in the range
- 33 of from about 65°C to about 180°C, (v) a thermoplastic
- 34 polymer having particles of about 1 to about 50
- 35 micrometers selected from the group consisting of
- 36 polyolefins, polyesters, and ethylene-vinyl acetate
- 37 copolymers, ethylene-methacrylic acid copolymers, and
- 38 ethylene-acrylic acid copolymers and which melts in
- 39 the range of from about 65°C to about 180°C; or (vi) a
- 40 natural wax; and
- 41 b) a water soluble or dispersible colorant;
- 42 wherein said water-soluble transferable material is
- 43 capable of transferring and adhering the transferable
- 44 colorant composition of the invention from a front
- 45 surface of a substrate support upon the application of
- 46 heat energy to the rear surface of the substrate, said
- 47 transferable colorant composition strips from said
- 48 front surface of the substrate by liquefying and
- 49 releasing from said substrate when heated, said
- 50 liquefied transferable colorant composition providing
- 51 adherence to a receptor element by flowing onto said
- 52 receptor element and solidifying thereon.
  - 1 24. A method of applying an image to a receptor
- 2 element which comprises the steps of:
- 3 (A) applying a water-soluble or dispersible
- 4 transferable colorant composition to a substrate, said
- 5 transferable colorant composition comprising:
- 6 (a) a transfer material having a melting point of
- 7 at least  $65^{\circ}\text{C}$  and comprising at least one of (i)
- 8 particles of a thermoplastic polymer having dimensions
- 9 of about 1 to about 50 micrometers, from about 10 to
- 10 about 50 weight percent of a film forming binder,
- 11 based upon the weight of the thermoplastic polymer,

- and optionally from about 0.2 to about 10 weight percent of a fluid viscosity modifier, based on the weight of the thermoplastic polymer, (ii) about 15 to about 80 percent by weight of a film-forming binder selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 17 85 to about 20 percent by weight of a powdered 18 selected from thermoplastic polymer 19 consisting of polyolefins, polyesters, polyethylene, 20 polyamides, waxes, epoxy polymers, ethylene-acrylic 21 ethylene-vinyl copolymers, and acetate 22 acid copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the 24 range of from about 65°C to about 180°C and the 25 powdered thermoplastic polymer comprises particles of 26 about 1 to about 50 micrometers, (iii) a film forming 27 binder selected from the group consisting of ethyleneacrylic acid copolymers having particles of about 1 to about 50 micrometers, polyolefins, and waxes and which 30 melts in the range of from about 65°C to about 180°C, 31 (iv) a thermoplastic polymer having particles of about 32 1 to about 50 micrometers selected from the group consisting of polyolefins, polyesters, and ethylenevinyl acetate copolymers and which melts in the range of from about 65°C to about 180°C, (v) a thermoplastic 36 polymer having particles of about 1 to about 50 37 micrometers selected from the group consisting of 38 polyolefins, polyesters, and ethylene-vinyl acetate 39 copolymers, ehtylene-methacrylic acid copolymers, and 40 ethylene-acrylic acid copolymers and which melts in 41 the the range of from about 65°C to about 180°C; or 42 (vi) a natural wax; and 43
  - 44 (b) a colorant;

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45 (B) positioning a surface of said substrate 46 having the transferable colorant composition thereon

against said receptor element, and

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- 48 (C) applying heat to the rear surface of said
- 49 substrate to transfer said transferable colorant to
- 50 said receptor element.
- 1 25. The method of claim 24, with the proviso that the
- 2 said colorant is not heat activated or sublimated.
- 1 26. The method of claim 24, wherein in step (A) said
- 2 image is applied to said substrate by a paint brush,
- 3 pen, finger painting, air brush, or an ink-jet
- 4 printer.
- 1 27. A kit comprising:
- 2 (A) at least one container having a water-
- 3 soluble or dispersible transferable colorant
- 4 composition, said transferable colorant composition
- 5 comprises:
- 6 (a) a water-soluble transfer material having a
- 7 melting point of at least 65°C and comprising at
- 8 least one of (i) particles of a thermoplastic
- 9 polymer having dimensions of about 1 to about 50
- 10 micrometers, from about 10 to about 50 weight
- 11 percent of a film forming binder, based upon the
- 12 weight of the thermoplastic polymer, and
- optionally from about 0.2 to about 10 weight
- 14 percent of a fluid viscosity modifier, based on
- the weight of the thermoplastic polymer, (ii)
- about 15 to about 80 percent by weight of a film-
- forming binder selected from the group consisting
- of ethylene-acrylic acid copolymers, polyolefins,
- 19 and waxes and from about 85 to about 20 percent
- by weight of a powdered thermoplastic polymer

  selected from the group consisting as
- selected from the group consisting of polyolefins, polyesters, polyethylene
- polyolefins, polyesters, polyethylene, polyamides, waxes, epoxy polymers, ethylene-
- 24 acrylic acid copolymers, and ethylene-vinyl

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- acetate copolymers, wherein each of said filmforming binder and said powdered thermoplastic polymer melts in the range of from about 65°C to about 180°C and the powdered thermoplastic polymer comprising particles of about 1 to about 50 micrometers, (iii) a film forming binder selected from the group consisting of ethylene-acrylic acid copolymers having particles of about 1 to about 50 micrometers, polyolefins, and waxes and which melts in the range of from about 65°C to about 180°C, (iv) a thermoplastic polymer having particles of about 1 to about 50 micrometers from group consisting selected the ethylene-vinyl polyolefins, polyesters, and acetate copolymers and which melts in the range from about 65°C to about 180°C, thermoplastic polymer having particles of about 1 to about 50 micrometers selected from the group polyolefins, polyesters, consisting of copolymers, ethyleneacetate ethylene-vinyl methacrylic acid copolymers, and ethylene-acrylic acid copolymers and which melts in the range of from about 65°C to about 180°C; or (vi) a natural wax; and
- 49 (b) a water soluble or dispersible colorant;
- 50 (B) at least one application means for applying
- 51 said transferable colorant composition to a substrate;
- 52 and
- 53 (C) optionally at least one substrate and/or at
- 54 least one receptor element.
- 1 28. A transferable liquid, aqueous colorant
- 2 composition, which comprises:
- a) a water-soluble transfer material having a
- 4 melting point of at least 65°C and comprising at least
- 5 one of (i) particles of a thermoplastic polymer having

dimensions of about 1 to about 50 micrometers, from about 10 to about 50 weight percent of a film forming binder, based upon the weight of the thermoplastic polymer, and optionally from about 0.2 to about 10 weight percent of a fluid viscosity modifier, based on the weight of the thermoplastic polymer, (ii) about 15 to about 80 percent by weight of a film-forming binder 13 selected from the group consisting of ethylene-acrylic acid copolymers, polyolefins, and waxes and from about 14 to about 20 percent by weight of a powdered 15 16 thermoplastic polymer selected from the consisting of polyolefins, polyesters, polyethylene, 17 polyamides, waxes, epoxy polymers, ethylene-acrylic 18 19 acid copolymers, and ethylene-vinyl acetate 20 copolymers, wherein each of said film-forming binder and said powdered thermoplastic polymer melts in the 21 range of from about 65°C to about 180°C and the 22 powdered thermoplastic polymer comprises particles of 23 about 1 to about 50 micrometers, (iii) a film forming 24 25 binder selected from the group consisting of ethyleneacrylic acid copolymers having particles of about 1 to about 50 micrometers, polyolefins, and waxes and which 27 28 melts in the range of from about 65°C to about 180°C, (iv) a thermoplastic polymer having particles of about 29 1 to about 50 micrometers selected from the group 30 consisting of polyolefins, polyesters, and ethylene-31 vinyl acetate copolymers and which melts in the range of from about 65°C to about 180°C, (v) a thermoplastic polymer having particles of about 1 to about 34 micrometers selected from the group consisting 35 36 polyolefins, polyesters, and ethylene-vinyl acetate 37 copolymers, ethylene-methacrylic acid copolymers, and ethylene-acrylic acid copolymers and which melts in 38 the range of from about 65°C to about 180°C; or (vi) a 39 40 natural wax; and 41 b) a water soluble or dispersible colorant; and

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#### 42 c) water.

- 1 29. The transferable liquid of claim 28, wherein said
- 2 colorant is selected from the group consisting of
- 3 pigments, dyes, and inks.
- 1 30. A water-soluble colorant composition, which
- 2 comprises:
- 3 a) a water-soluble material having a melting
- 4 point of at least 65°C and comprising at least one of
- 5 (i) particles of a thermoplastic polymer having
- 6 dimensions of about 1 to about 50 micrometers, from
  - about 10 to about 50 weight percent of a film forming
- 8 binder, based upon the weight of the thermoplastic
- 9 polymer, and optionally from about 0.2 to about 10
- 10 weight percent of a fluid viscosity modifier, based on
- 11 the weight of the thermoplastic polymer, (ii) about 15
- 12 to about 80 percent by weight of a film-forming binder
- 13 selected from the group consisting of ethylene-acrylic
- 14 acid copolymers, polyolefins, and waxes and from about
- 15 85 to about 20 percent by weight of a powdered
- 16 thermoplastic polymer selected from the group
- 17 consisting of polyolefins, polyesters, polyethylene,
- 18 polyamides, waxes, epoxy polymers, ethylene-acrylic
- 19 acid copolymers, and ethylene-vinyl acetate
- 20 copolymers, wherein each of said film-forming binder
- 21 and said powdered thermoplastic polymer melts in the
- 22 range of from about 65°C to about 180°C and the
- 23 powdered thermoplastic polymer comprising particles of
- 24 about 1 to about 50 micrometers, (iii) a film forming
- 25 binder selected from the group consisting of ethylene-
- 26 acrylic acid copolymers having particles of about 1 to
- 27 about 50 micrometers, polyolefins, and waxes and which
- 28 melts in the range of from about 65°C to about 180°C,
- 29 (iv) a thermoplastic polymer having particles of about
- 30 1 to about 50 micrometers selected from the group

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- 31 consisting of polyolefins, polyesters, and ethylene-
- 32 vinyl acetate copolymers and which melts in the range
- 33 of from about 65°C to about 180°C, (v) a thermoplastic
- 34 polymer having particles of about 1 to about 50
- 35 micrometers selected from the group consisting of
- 36 polyolefins, polyesters, and ethylene-vinyl acetate
- 37 copolymers, ethylene-methacrylic acid copolymers, and
- 38 ethylene-acrylic acid copolymers and which melts in
- 39 the range of from about 65°C to about 180°C; or (vi) a
- 40 natural wax; and
- 41 b) a water soluble or dispersible colorant.
- 1 31. A method of applying an image to a receptor
- 2 element which comprises the steps of:
- 3 (A) applying a water-soluble or dispersible
- 4 colorant composition to a receptor element, said
- 5 colorant composition comprising:
- 6 (a) a material having a melting point of at least
- 7 65°C and comprising at least one of (i) particles of a
- 8 thermoplastic polymer having dimensions of about 1 to
- 9 about 50 micrometers, from about 10 to about 50 weight
- 10 percent of a film forming binder, based upon the
- 11 weight of the thermoplastic polymer, and optionally
- 12 from about 0.2 to about 10 weight percent of a fluid
- 13 viscosity modifier, based on the weight of the
- 14 thermoplastic polymer, (ii) about 15 to about 80
- 15 percent by weight of a film-forming binder selected
- 16 from the group consisting of ethylene-acrylic acid
- 17 copolymers, polyolefins, and waxes and from about 85
- 18 to about 20 percent by weight of a powdered
- 19 thermoplastic polymer selected from the group
- 20 consisting of polyolefins, polyesters, polyethylene,
- 21 polyamides, waxes, epoxy polymers, ethylene-acrylic
- 22 acid copolymers, and ethylene-vinyl acetate
- 23 copolymers, wherein each of said film-forming binder
- 24 and said powdered thermoplastic polymer melts in the

- 25 range of from about 65°C to about 180°C and the
- 26 powdered thermoplastic polymer comprises particles of
- 27 about 1 to about 50 micrometers, (iii) a film forming
- 28 binder selected from the group consisting of ethylene-
- 29 acrylic acid copolymers having particles of about 1 to
- 30 about 50 micrometers, polyolefins, and waxes and which
- 31 melts in the range of from about 65°C to about 180°C,
- 32 (iv) a thermoplastic polymer having particles of about
- 33 1 to about 50 micrometers selected from the group
- 34 consisting of polyolefins, polyesters, and ethylene-
- 35 vinyl acetate copolymers and which melts in the range
- 36 of from about 65°C to about 180°C, (v) a thermoplastic
- 37 polymer having particles of about 1 to about 50
- 38 micrometers selected from the group consisting of
- 39 polyolefins, polyesters, and ethylene-vinyl acetate
- 40 copolymers, ehtylene-methacrylic acid copolymers, and
- 41 ethylene-acrylic acid copolymers and which melts in
- 42 the the range of from about 65°C to about 180°C; or
- 43 (vi) a natural wax; and
- 44 (b) a colorant;
- 45 (B) positioning a front surface of a non-stick
- 46 sheet against said receptor element over the area on
- 47 which said water-soluble colorant composition is
- 48 applied, and
- 49 (C) applying heat to a rear surface of said non-
- 50 stick sheet; and
- 51 (D) removing said non-stick sheet from said
- 52 receptor element.
- 1 32. The method of claim 31, wherein said colorant is
- 2 not heat activated or sublimated.
- 1 33. The method of claim 31, wherein in step (A) said
- 2 image is applied to said substrate by a paint brush,
- 3 pen, finger painting, airbrush, or an ink jet printer.

FIG. 1

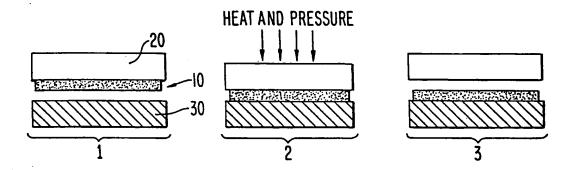
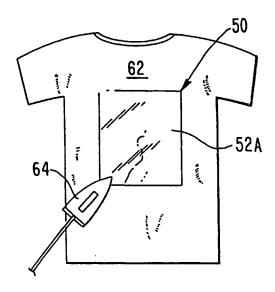


FIG. 2



SUBSTITUTE SHEET (RULE 26)

int tional Application No PCT/US 99/17544

A. CLASSIFI IPC 7	CATION OF SUBJECT MATTER 841M5/03 C09D11/02 C09B67/20		
Assertion to l	international Patent Classification (IPC) or to both national classification of	and IPC	
B. FIELDS S Minimum doc IPC 7	rumentation searched (classification system followed by classification system $841M - 009D - 009B$	mbols)	
	on searched other than minimum documentation to the extent that such o		cned
Electronic da	ata base consulted during the international search (name of data base ar	nd, where practical, search terms used)	
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevan	nt passages	Relevant to claim No.
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X FL	urther documents are listed in the continuation of box C.	X Patent family members are lister	d in annex.
'A" docucon 'E" earlite filin 'L" docuwhicita 'O' docuoth 'P" docu	categories of cited documents:  Iment defining the general state of the art which is not sidered to be of particular relevance or document but published on or after the international g date  Iment which may throw doubts on priority claim(s) or chi is cited to establish the publication date of another action or other special reason (as specified)  Imment referring to an oral disclosure, use, exhibition or er means  Imment published prior to the international filing date but or than the priority date claimed  The actual completion of the international search	To later document published after the im or priority date and not in conflict with cited to understand the principle or tinvention.  X** document of particular relevance; the cannot be considered novel or cannivolve an inventive step when the cannot be considered to involve an document of particular relevance; the cannot be considered to involve an document is combined with one or ments, such combination being obvin the art.  Authorized officer.	heary underlying the claimed Invention of be considered to locument is taken alone or claimed invention inventive step when the more other such documious to a person skilled int tamily search report
Name a	nd mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  Fax: (+31-70) 340-3016	Authorized officer  Ketterer, M	

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ational application No. PCT/US 99/17544

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
1. X Claims Nos.: 30 (partially) because they relate to subject matter not required to be searched by this Authority, namely:
see FURTHER INFORMATION sheet PCT/ISA/210
Claims Nos.:     because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
Claims Nos.:     because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.

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## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.1

Claims Nos.: 30 (partially)

Claim 30 defines water-soluble colorant compositions in a broad and general sense. There is no limitation as in the other compound claims 1, 23 and 28 focussed to the heat transfer technique. Claim 30 was therefore searched only partially concerning colorant compositions useful or used in the field of heat transfer recording.

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